STRENGTHENING ISSUES FOR HIGH-TEMPERATURE NI-BASED ALLOYS FOR USE IN USC STEAM CYCLES

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ABSTRACT

The demand for higher efficiency and reduced emissions in coal-fired power boilers will result in the use of higher steam temperatures and pressures. A significant materials effort is required to reach a target steam condition of 760°C/35MPa. These new Ultrasupercritical (USC) units will require the use of nickel-based superalloys in both the superheater tubing and the header piping. Two nickel-based alloys of primary interest for these USC boilers are a controlled chemistry version of the nominally solid solution strengthened alloy 617, CCA617, and a newly developed age hardenable alloy, Inconel ® 740. Long-term creep strength will be one of the primary limiting factors in the use of these alloys. Based on extrapolation of the temperature for rupture in 100,000 hours at 100MPa, the creep strength temperature limit is 700°C for alloy 617, estimated at 720 to 730°C for CCA617, and estimated at 780 to 790°C for Inconel ® 740. A fundamental understanding of the microstructural evolution and stability of these alloys during aging and creep is needed to: (a) understand the differences in creep strength between CCA617 and standard 617, (b) determine if this strength difference is a short-term phenomenon or will be sustained for lifetimes of 100,000 hours and beyond, (c) understand the complex precipitation and growth behavior between gamma prime and eta phase precipitates in alloy 740, and (d) use this information to help define the maximum use temperatures for alloy 740. Current research on CCA617 indicates that the formation of an appreciable volume of gamma prime precipitates is the origin for the strength differences between the CCA617 and standard 617. However, rapid coarsening and possible dissolution of these precipitates limits the effectiveness of this type of hardening after short-term aging at 800°C and this may extend to lower temperatures as well. In alloy 740, a large difference has been observed in the gamma prime precipitate growth between 750 and 800°C. The formation of eta phase at the expense of the gamma prime precipitates has also been observed after relatively short aging and creep test times.

INTRODUCTION

Increased efficiency of coal-fired power boilers can be achieved by increasing steam temperatures and pressures into the ultrasupercritical (USC) steam regime. Concurrently, USC steam conditions will reduce power-plant emissions. These driving forces have lead to the formation of a USC Steam Boiler consortium made up of U.S. boiler manufactures and research organizations funded through the U.S. Department of Energy (DOE) and the Ohio Coal Development Office (OCDO). The objective of this consortium is to identify, evaluate, and qualify the materials needed for operating a USC steam boiler at a target steam condition of 720°C/760°C/35MPa [1]. Oak Ridge National Laboratory (ORNL) is responsible for producing the mechanical properties database needed to design and operate a boiler within the scope of the project [2]. To meet the long-term creep strength requirements at these temperatures and pressures, these new USC units will require the use of nickel-based superalloys in both the superheater tubing and the header piping. Two nickel-based alloys of primary interest are CCA617 and Inconel ® 740. Understanding the microstructural changes in these alloys at temperatures typical of service conditions is fundamental to evaluating and understanding their observed long-term mechanical properties. ORNL and the University of Cincinnati have been jointly working together to characterize the microstructural changes in these materials by studying both aged and creep-tested material [3].

CCA617

Alloy 617 is nominally a solid solution strengthened Ni-based superalloy. Mo and Co provide solid solution strengthening, and $M_{23}C_6$ carbides provide a strength contribution through precipitation hardening. Additionally, Ni and Al form the gamma prime (γ’) intermetallic over a range of temperatures, which provides strengthening over and above solid solution strengthening. Extensive creep-rupture databases exist for alloy 617. As typical for creep-rupture data, scatter due to testing, processing, and heat-to-heat variations are observed. With the emphasis on the material for use at 600°C to 800°C, a controlled chemistry version of 617, called CCA617, was produced to eliminate the low end of the 617 scatter band for improved creep resistance below 800°C. The chemistry range/limits on C, Si, Mn, S, Al, B, Co, Cr, Cu, Ti, and Fe were tightened compared to standard 617 [4]. Current creep-rupture testing on CCA617 at ORNL, figure 1, shows an improvement in creep strength compared to the 617 database below 700°C. Extrapolating for rupture in 100,000 hours, the strengths of the 617 and CCA617 appear to converge between 700 and 750°C.

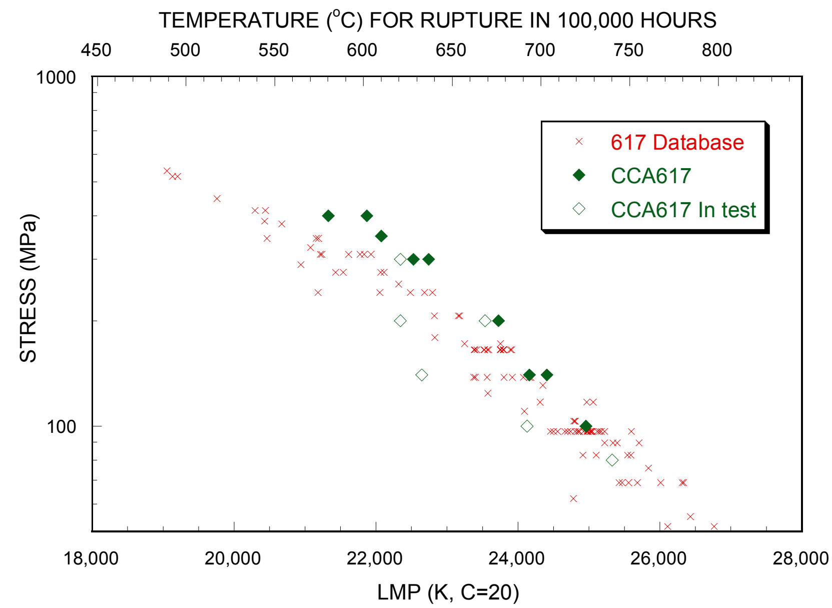

Figure 1. Larson-Miller Parameter (LMP) vs. Stress for CCA617 (open diamond is still in test) compared with the 617 historical database. Upper abscissa gives extrapolation for temperature for rupture in 100,000 hours.

To understand the origins of the difference in creep strength below 750°C for the CCA617 and standard 617, electron microscopy studies were performed on CCA617 aged at 700, 750, and 800°C for times up to 3,000 hours. The gamma prime (γ') intermetallic precipitate was identified at all temperatures. Figure 2 shows the calculated volume percent of γ' versus time for all three temperatures [3]. At 700 and 750°C, appreciable amounts (in excess of 8 vol. %) of γ' were identified. However, rapid coarsening and possible dissolution of these precipitates after aging for 3,000 hours at 800°C limits the effectiveness of this type of hardening at 800°C. This can be clearly seen in the TEM images of the 3,000 hour aged specimens in figure 3. Thus, it appears that one possible reason for the increase in creep strength of the CCA617 compared to the 617 below 730°C is the precipitation of gamma prime, but at higher temperatures the precipitates coarsen rapidly and do not provide additional strengthening [4]. Additional studies continue on longer-term aged material (10,000+ hours) and creep-tested specimens to further understand the precipitation behavior of CCA617.

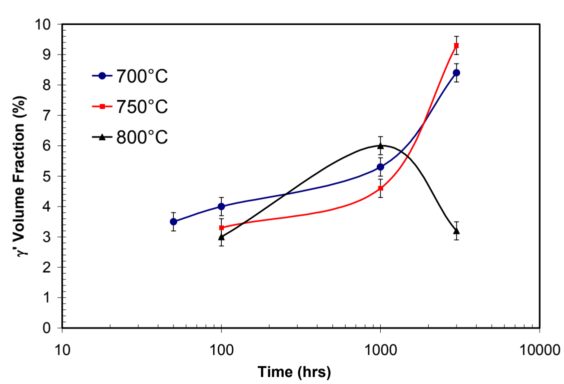

Figure 2. Calculated volume percent gamma prime with temperature for aged CCA617 (Based on TEM foil with a thickness of 100nm)

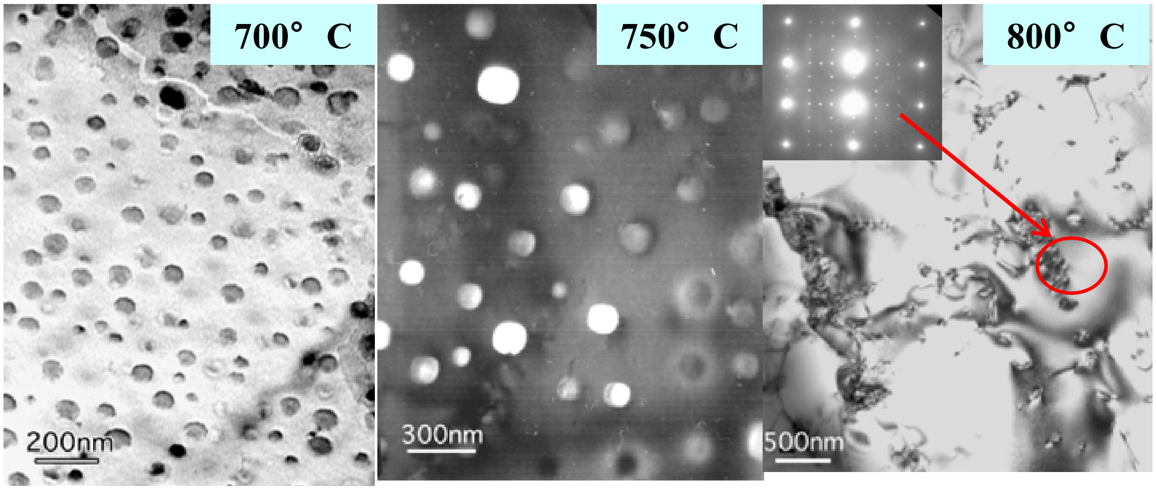

Figure 3. TEM images of gamma prime (γ') precipitates in CCA617 after aging at 700°C, 750°C, and 800°C for 3,000 hours.

Inconel 740

The newly developed Inconel ® alloy 740 is a Ni-based superalloy which is primarily strengthened by the precipitation of gamma prime (γ'), and additionally solid solution-strengthened by Co. The low Mo content of the alloy promotes good coal ash corrosion resistance and the Cr content (25 wt%) was increased above 617 (20% Cr) for good oxidation resistance to at least 750°C. The creep strength of alloy 740 is much greater than that of alloy 617, as shown by the Larson Miller plot in figure 4. As with the CCA617, aging studies are being conducted at 700, 750, and 800°C to evaluate the microstructure and mechanical properties of the alloy. This is important because limited data are available on the aging behavior and microstructural evolution in this alloy.

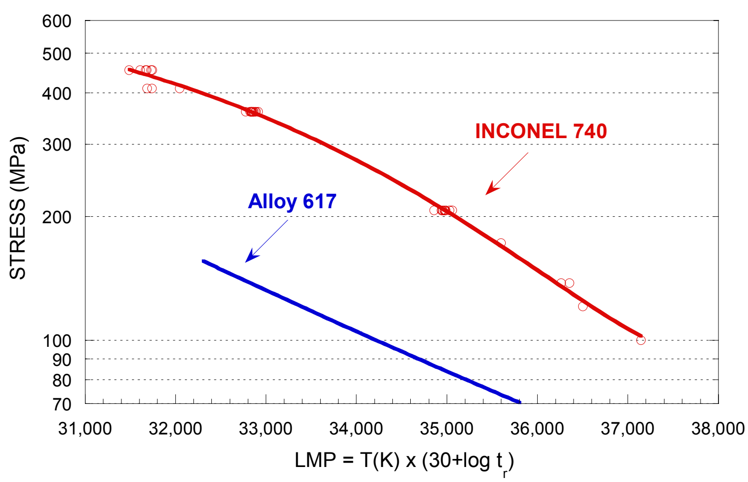

Figure 4. Larson-Miller Parameter (LMP) vs. Stress for Inconel 740 Rupture lives compared with standard 617.

The results of room temperature tensile tests (UTS and YS) after aging on alloy 740 are shown in figure 5. After aging for 1,000 hours at 700 and 750°C, the material reaches a maximum ultimate tensile strength, which appears to hold to 3,000 hours. In contrast, at 800°C, a maximum tensile strength is achieved at 300 hours and the strength decreases continually to 3,000 hours. The strength after aging for 3,000 hours at 800°C is roughly 15% less than the strength after aging for 3,000 hours at 700 and 750°C. Scanning electron microscopy evaluation of the 750 and 800°C 3,000 hour aged specimens reveal microstructural differences. For the 750°C aged material, grain boundary carbides are present, but the material is relatively clean. In contrast, after aging at 800°C, large plate-like precipitates (white) originating at the grain and twin boundaries and extending into the grains are evident. These have been identified as eta (η) phase. Further studies have shown that eta phase forms at the expense of the gamma prime precipitates (primary strengthening phase), thus reducing the room temperature strength of the alloy after relatively short aging periods at 800°C. More studies are ongoing for longer aging times and on creep tested materials to evaluate the complex precipitation and growth behavior between gamma prime and eta phase precipitates.

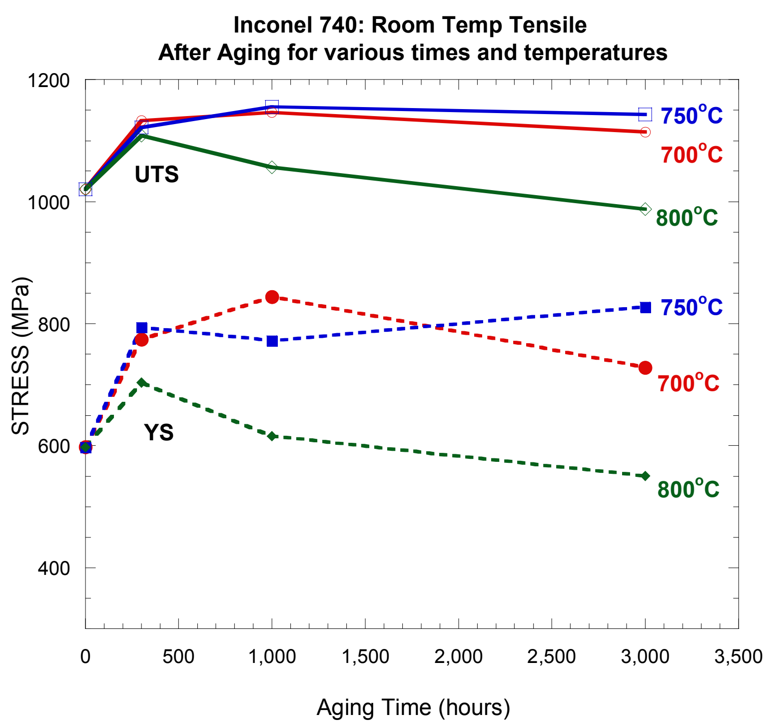

Figure 5. Room temperature ultimate tensile strength (UTS) and yield strength for Inconel 740 aged at various times and temperatures.

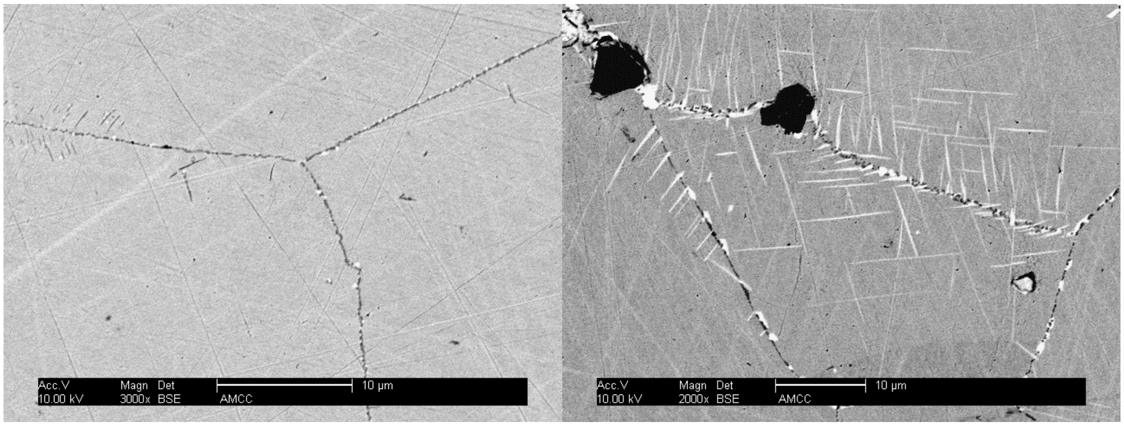

Figure 6. SEM image of Inconel 740 after aging at 750C for 3,000 hours showing the absence of large eta phase precipitates (Left) and after aging at 800C for 3,000 hours showing plate-shaped eta phase precipitates (Right)

CONCLUSIONS

Aging studies are being conducted by ORNL and the University of Cincinnati to support the USC Steam Boiler Consortium. The goal of the work is to characterize the microstructural changes of candidate USC boiler materials at expected service temperatures. These studies will be used to better understand long-term mechanical properties, including creep-strength differences between CCA617 and standard 617 and the loss of tensile strength after long-term high-temperature exposure in Inconel 740. Current research on CCA617 indicates that the formation of an appreciable volume of gamma prime precipitates is the origin for the strength differences between the CCA617 and standard 617. However, rapid coarsening and possible dissolution of these precipitates limits the effectiveness of this type of hardening after short-term aging at 800°C. In Inconel alloy 740, the formation of eta phase reduces the strength of the alloy after relatively short aging at 800°C.

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